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PHOTOELECTRET PROPERTIES AND HIGH-FIELD POLARIZATION IN CHALCOGENIDE GLASSES AND THIN FILMS

E. Skordeva

Institute of Solid State Physics, Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee blvd, 1784 Sofia, Bulgaria

The paper is dedicated to the 90th anniversary from the birth of my father, the late Prof. Razum Andreichin. It is dedicated also to the 20th commemoration from the death of the Academician Georgy Nadjakov, the discoverer of the photoelectret state (PES). A short historical review on the invention of PES is followed by a brief presentation of the matter of the photoelectret state and the high-field polarization. The most part of the results obtained from Prof. Andreichin and co-workers during investigations of PES in chalcogenide glasses, mainly As₂S₃ and As₂S₃-based ones, is summarized.

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1. Introduction

1.1. Short historical presentation

The term "electret" was introduced at the end of the 19th century by O. Heaviside [1] as a counterpart of the term "magnet". The first representative of the great family of the electrets was the thermoelectret, discovered by Eguchi [2]. The electrets family contains nowadays a number of different members — thermoelectrets, photoelectrets, thermophotoelectrets, radioelectrets, magnetolectrets etc. One of them, the photoelectret, was discovered by the Bulgarian physicist G. Nadjakov in 1937 [3]. In that time Prof. Andreichin was a Ph.D. student of Prof. Nadjakov. He kept the interest to that matter all his life. There was a strong "photoelectret" school in Bulgaria led by Prof. Nadjakov (Chetkarov, Andreichin, Kashukeev, Antonov et al). A great deal of the contribution to the photoelectret state investigations has the Russian School (Fridkin, Zheludev, Adirovich, Tartakovskii etc). There was a group of researchers in India (Pillai, Jain et.al.) which has also contributed to the investigation of the photoelectret state. Researchers from all over the world have worked in this scientific region because of the large application possibilities it gives (PES is widely used nowadays in the technique - in the electrophotography, xerography, electrofax technique etc.).

The first material in which the photoelectret state was proved was polycrystalline sulfur. Later this state was found in many other wide-band-gap materials, crystalline or amorphous. Several reviews on photoelectrets are listed in references [4-7]. The first publication on photopolarization and photoelectret state in vitreous semiconductors was reported in 1962 by B. Kolomiets and V. Lyubin [8]. In the same time investigations have been carried out in the laboratory of Prof. Andreichin in Sofia. Their first results concerning the existence of a pronounced photoelectret state in vitreous arsenic sulfide were published in 1965 [9]. A great part of the investigations on the photoelectret state in amorphous chalcogenide has been summarized by R. Andreichin in Ref. [10].* In the present review published [11-16] and unpublished results of the investigation on photoelectret properties of As₂S₃-based glasses and thin films carried out in the laboratory of Prof. Andreichin are used.

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1.2. Photoelectret state

The photoelectret state is characterized by a prolonged preservation in darkness of the photopolarization called photoelectret polarization. The photopolarization P is the total polarization obtained for an illuminated sample. The analysis of the polarization/depolarization phenomena leads to a conclusion that they consist of three components (related to 3 processes):

(a) *A dark high-field polarization*, which is independent on the illumination. It disappears for a comparatively short time. The process begins at once after the removal of the field. This polarization is supposed to be caused by relatively shallow traps in the semiconductor.

Wide-band-gap amorphous semiconductors manifest the high-field polarization in darkness with both blocking and injecting electrodes. The latter show that the dark polarization is not only surface, but also bulk phenomena.

(b) *A high-field light polarization*. It has the same character as the dark one but the initial current and the accumulated charge are greater. The corresponding depolarization begins also immediately after removal of the field but it decays more slowly in darkness. This polarization is probably due to a higher concentration of filled levels at the same (or slightly greater) depth as the dark polarization.

Both high-field depolarizations are supposed to be the consequence of thermal recombination.

(c) *Photoelectret polarization* – the permanent polarization of samples kept in darkness. In this process the charge is stored for a long time and deep traps are filled. The depolarization at room temperature after removal of the field begins only when the semiconductor is illuminated again.

It is hard to trace a sharp boundary between light and photoelectret polarization in any real photoelectret and moreover for the disordered ones: the zone between the shallow and deep states is smeared. However, as will be pointed later, a relative decision of this problem can be found.

2. Experimental

Since the formation of the photoelectret state requires a wide band gap, different type of electrometers must be used. The first used in the laboratory electrometers were the constructed by the Academician G. Nadjakov mechanical ones. The kinetics of the polarization and depolarization was investigated using the electronic electrometers of the German Vakutronik and of the Keithley type.

Bulk samples in the form of plates 0.1-1 mm thick were investigated with both gap plane and sandwich type electrodes. Thin films evaporated on mica or teflon with a wide gap between the electrodes were also used.

In the early years of investigation of the electrical properties of the amorphous semiconductors it was believed that no problems with contacts or special effects associated with surfaces exist. Fritzsche has pointed that in several cases this statement is not right [17]. Very high contact resistances are usually encountered in wide gap (larger than 1.5 eV) amorphous semiconductors such as Se, As_2Se_3 , and As_2S_3 . E.g. when the electrode is allowed to oxidize before it is covered with the amorphous film, it gives rise to a larger contact resistance. In some cases a hole blocking contact is formed at larger biases ($V \sim 0.5$ volt) - the oxidized contact passes electrons from the metal into the amorphous semiconductor but not reverse. When the electrode, however, is a non-oxidizing metal, the low voltage ohmic region corresponds to the bulk resistance of the amorphous material [17]. The type of the contact is usually evaluated by measuring the $U(I)$ characteristics of the measured sample. The currents should be linear in field indicating the absence of space-charge limitations when electrical resistivity is the aim of the investigation. Another way to check the "reliable" contact provide the comparison of measured $I(T)$ curves obtained by increase and decrease of the temperature. The "hysteresis", however, can be also due to some experimental mistake.

In the light of the mentioned above difficulties it should be stressed that in any case it will be necessary to choose carefully the type of electrodes for any composition.

Our experience has shown that it is very hard to find ohmic contacts for the wide-band-gap semiconductors. Silver contacts are ohmic but diffusion into the sample occurs not only under illumination and heating but even at room temperature. Using gold is a little better. However diffusion of the contact material into the sample is observed by high temperatures. The aquadag contacts are ohmic (injecting) and have been used for bulk samples. Thin films however have been damaged (partially solved in the vicinity of the contact). These problems are not actual when polarization properties are studied. In fact, when using blocking electrodes, both dark and photopolarization are more clearly manifested and considerably stronger. Relatively good blocking contacts have been obtained by evaporating aluminum on the films and

bulk samples. Blocking electrodes have been also formed simply by pressing small metal lamellae to well polished bulk samples. Sometimes we put highly isolating spacers under the lamellae.

In some of the experiments a combination of one blocking and one injecting contacts was used.

3. Results

All of the investigated As_2S_3 -based samples have shown typical polarization/depolarization curves at room temperatures. A more detailed analysis of the kinetic of these curves has shown that they are multi-exponential and can be presented as a sum of several currents with different initial values and relaxation times [11]. For the depolarization currents

$$I_d(t) = \sum I_{oi} e^{-b_i t} \quad (1)$$

For polarization and depolarization in the dark the sum of the exponents can be satisfactorily reduced to a sum of two components, a rapid one and a slow one. In the case of injecting electrodes the first component decreases very rapidly. By depolarization under illumination the decay curve can be resolved into at least three components. The number of the components depends on the composition. The relaxation times remain almost the same even after keeping the sample for a long time Δt in darkness. The initial current I_0 depends on the polarization conditions and decreases with the time. An example of photodepolarization current expansion of As_2S_3 is presented in Table 1. The addition of Ag and Cu to As_2S_3 leads to a decrease of the number of the components and to changes in their relaxation times. The addition of Sn and Ge does not change significantly the kinetics, although the time constants differ with the compositions (e.g. $b_1 \approx 0.026$, $b_2 \approx 0.073$ and $b_3 \approx 0.354$ for $\text{As}_2\text{S}_3 + 1.5$ at.% Sn and $b_1 \approx 0.015$, $b_2 \approx 0.054$ and $b_3 \approx 0.14$ for $\text{As}_2\text{S}_3 + 2$ at.% Sn). The kinetics of the polarization and depolarization currents depends also on the technological pre-history of the samples.

Table 1. Kinetics of photodepolarization current of vitreous As_2S_3 .

Δt [hours]		0.5		24	95	P
I_{01} [a. u.]	106.3	132.6	95.5	91.3	69.2	88.3
I_{02} [a. u.]	1652	1245	959.8	745.7	477.1	1306
I_{03} [a. u.]	1227	877	687.7	609.6	376	1764.9
I_0 [a. u.]	2885	2136.6	1743	1446.6	922.3	3159.2
b_1	0.071	0.071	0.071	0.071	0.071	0.055
b_2	0.258	0.203	0.190	0.205	0.203	0.228
b_3	0.643	0.485	0.457	0.523	0.512	0.559
Q	22600	19900	17900	14000	9300	22800

$$Q = \sum_{i=1}^n Q_i = \sum_{i=1}^n \int_0^{\infty} I_{oi} e^{-b_i t} dt = \sum_{i=1}^n \frac{I_{oi}}{b_i} \quad (2)$$

Differences have been observed not only in the kinetics of the polarization/depolarization currents. Changes in the value of the polarization in dark (P_d) or in light (P_l) when new elements are added to the basic glass matrix have also been registered [12-15]. E.g., P_d and P_l shows an upward tendency with an increase in silver concentration and the photopolarization ($P_l - P_d$) decreases, like the photoconductivity [9].

$$P = U \frac{I_0 - I_1}{I_0} \quad (3)$$

A measure of the photodepolarization P can be the ratio I_{od}/I_{op} , or, even better, Q_d/Q_p . I_{od} and I_{op} are the initial currents of depolarization and polarization, Q_d and Q_p are the charges released by the depolarization and accumulated during the polarization, resp. Since a sharp boundary between light- and photoelectret- polarization cannot be drawn, the decay curve of the photoelectret charge $Q_d/Q_p(t)$ could be usable. When the ratio approaches a constant value, the polarization remaining is due solely to the photoelectret state (Fig. 1). Q_d/Q_p depends also on the composition of the electret (Table 2).

Table 2. Qd/Qp for bulk samples with different compositions.

		Sn			Cu				Ag		
At. %		1.5		2.5	0.5				0.5	1	2
Light	80	55	40	30	20	41	58	56	15	10	15
Dark	40				12	28	30	28	30	10	15

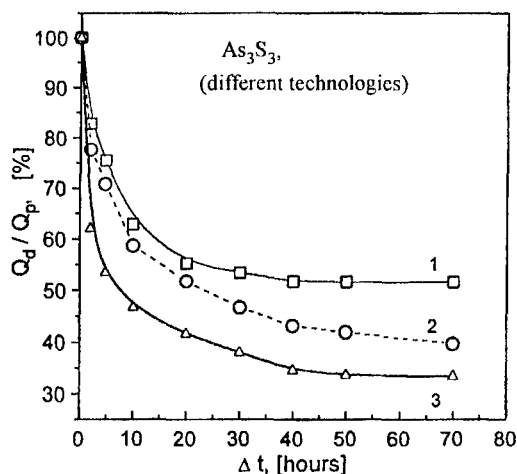


Fig. 1. Dependence of the photo-polarization on the time Δt for bulk samples obtained by different cooling technologies. Curve 1 - the ampoule with the melt was kept 24 hours at 200°C, curve 2 - the cooling was performed in the furnace, curve 3 - cooling in the air [16].

Powerful methods for investigation of the charge created in the deep traps of the electrets are those using thermally stimulated discharge. The method of thermally stimulated currents can be used and, also, the method of the thermally stimulated depolarization. In the latter the heated sample is cooled under illumination and applied voltage. Then on re-heating of the electret without applied voltage, the stored charge is released. The discharge $I(T)$ curves are registered as "glow peaks". The shape of these peaks is supposed to be similar to the uniform density of the previously stored in the traps charge. Although the position of the discharge peaks depends on the experimental details (applied voltage, spectral characteristics and intensity of the used light, the velocity of the temperature change etc.), a qualitative scheme of the deep band-gap-states distribution can be drawn. The bad side of this method is that it does not give a complete picture of the whole band structure but only of a small part of it.

Fig. 2 and 3 represent several discharge curves obtained using the method of the thermally stimulated depolarization. The curves are normalized toward 100% for the higher extremum in order to elucidate the differences in the shape and the position of the maxima. The shape of the obtained maxima varied with the composition, both with the amount and the type of the added to the arsenic sulfide metal. A rough evaluation of the parameters of the traps, that are potentially connected with these maxima, gives the values of 0.4-0.78 eV for the depth (from the top of the valence band) and a minimal concentration of the filled traps about 10^{11} . [12-15]. Similar results have been obtained by other authors in chalcogenide glasses when photoluminescence was investigated. The presence of two groups of levels: one close to the band edge, and another about 1 eV deep in chalcogenide glass has also been reported by Kolomiets. et. al. [18].

Photoelectret state and photopolarization have been found not only in the mentioned above materials. We have also observed them in glasses of the $\text{As}_2\text{S}_3\text{-As}_2\text{O}_3$, $\text{As}_2\text{S}_3\text{-GeS}_2$, $\text{As}_2\text{S}(\text{Se})_3\text{-Ge}_2\text{S}(\text{Se})_3$ and other systems. Investigation of thin films evaporated from these glasses has shown that, although less pronounced, the same polarization phenomena as in bulk samples are present. Evaporated layers of the same composition as bulk materials show much weaker photoelectret properties. However, for technological reasons thin films are successfully used in the electrophotography.

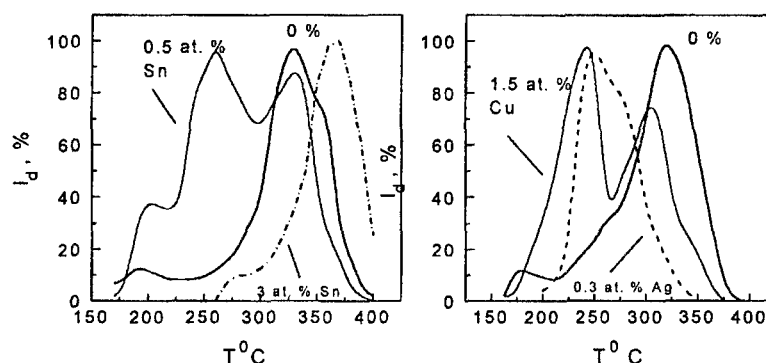


Fig. 2. Depolarization curves obtained for bulk As_2S_3 -based glasses with different additives.

4. Discussion

The photoelectret properties of As_2S_3 -based glasses are characterized by all the common features of the crystalline photoelectrets: (1) For a constant light intensity the accumulated charge Q depends linearly on the applied field up to a certain value (e.g. 3 kV/cm) and then tends to saturation; (2) For a constant external electrical field Q is proportional to the illumination; (3) For both constant field and illumination Q depends initially linearly on the irradiation time, after which becomes saturated; (4) The reciprocity law is obeyed to a certain high value of the radiant energy. The difference between the crystalline and amorphous photoelectrets consists mainly in the lack of a broad interval without traps in the latter ($\Delta E > 0.4$ eV is needed, according to the photoelectret theory [5]). It is obvious, however, that despite of the hypothesis about the large area of traps distribution in the band gap in the amorphous semiconductors, the presence of photoelectret state is possible. The undoubted result obtained by the summarized above investigations is the non-uniform distribution of the traps in the band gap.

Shallow traps are related to the dark and light high-field polarization. The results of the performed current expansion allow to suppose different trapping levels for the different current components. They may differ either in depth, or in mechanisms of accumulation, trapping cross-section etc. It is not necessary to connect these traps with the band tails, but it is very probable that they are. As_2S_3 glasses cooled with different rates have shown, differences in the grade of their PES, as well as in the amount of P and Q_d/Q_p (Fig. 1, the cooling rates are respectively $v_1 < v_2 < v_3$). Long time annealing or low rate of cooling lead to greater order and decrease of the band tails. When metal additions are included in the glass matrix of As_2S_3 , the medium and long-range order are also damaged. The addition of Ag disturbs the chain-like and layer-like structure. New shallow traps become active and the accumulated by the polarization charge is released faster. The addition of Sn may help the formation of longer layers and decrease the amount of shallow traps. The band tails decrease and the gap between them and the deep traps increases. As a result the photoelectret properties of the materials becomes better pronounced. The change of the composition leads to changes of the size of the semiconductor band gap. This process can also increase or decrease the assumed gap between the deep traps and the next ones taking part into the conductivity. Not only the position but also the density of the mentioned traps could be changed in a similar way.

The results of the thermally stimulated depolarization have shown that somewhere around the middle of the band gap a non-uniform distribution of deep traps also exists. Probably all the intermediate states are localized and do not allow a thermal recombination to the bands until a sufficient energy is absorbed. However, the attempt to do a spectral dependence of the photopolarization at room temperature has shown that the polarization considerably increases only when the photon energy is greater than the band gap. This discrepancy might not be connected only with the slight intensity of the used light (see the last paragraph of this section).

The deep gap states might originate from dangling bonds, defects and random deviations from the network structure. As_2S_3 has a local structure spread to the dimensions of the middle-range order. Independently on the fact are the As_2S_3 -pyramids connected simply in layers or clustered, many uncompensated free states can be present at their ends. The addition of new elements leads to the formation

of new structural units and changes the charge and the amount of those states. That is the reason for the different behavior of the glasses containing Ag and Sn. In both cases, however, the stoichiometry was disturbed. As a result the position of the thermostimulated depolarization peaks changes. (All the experimental conditions were equal).

In the same experimental conditions the depolarization curves of As_2S_3 - As_2O_3 glasses have not shown any significant changes with the composition. This is probably due to the fact that both molecular components are stoichiometric, isomorphic and the parameters of the local order do not differ essentially.

The thin evaporated films are essentially more disordered than the parent glasses. Many new shallow traps are formed in their band gap and the accumulated during the polarization charge is easily released.

Several authors have supposed a relation between the dark conductivity and the position and height of the corresponding peak of the depolarization current [19, 20]. According to P. Muller, if the depolarization is caused by equilibrium charge carriers the position (temperature of the maximum) and the height of the TSD peak can be predicted. P. Muller has supposed that the bulk conductivity determines accumulation or depletion of charges in the surface, adjacent to the blocking electrodes regions. Although such a model seems not applicable for our experimental results, it is worth to turn the attention of the future investigations towards the correctness of all types of interpretation of the TSD results. Moreover, since this paper is written as a review of works performed in the past, it would be advisable to use new contemporary methods to elucidate all the discrepancies and unclear items.

5. Conclusions

The present review has shown that the polarization and photoelectret phenomena in As_2S_3 -based amorphous semiconductors do not differ phenomenologically from those in the corresponding crystalline semiconductors. The explanation of this phenomena based on the band theory for crystalline or amorphous semiconductor, however, meets with some difficulties and requires much more investigations.

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